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Engineering strontium titanate-based photocatalysts for green hydrogen generation: Recent advances and achievements

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ABSTRACT

The production of fuels from renewable energy sources such as sunlight offers a promising approach to store chemical energy. Apart from fundamental improvements, innovative ideas on the design of photocatalytic systems can also advance solar energy utilization by integrating complementary technologies to utilize the solar spectrum more efficiently. This review highlights the recent developments of the new $SrTiO_3$ based photocatalytic systems and other approaches for enhanced separation of photogenerated charge carriers towards surface catalyzed reactions. Based on our survey, $SrTiO_3$ based photocatalysts are one type of widely explored materials for solar water splitting in recent years both from the fundamental approach and for commercial applications. Thus, we intend to summarize the details of $SrTiO_3$ based photocatalysts from starting to advanced research and interesting information of small-scale research to the larger-scale application along with historical progression.

1. Introduction

Finding a modern and alternative way to produce renewable energy is very important due to the increasing demand for global electrical power consumption, environmental problems and the depletion of natural sources [1–3]. Hydrogen is recognized as a crucial zero-emission fuel in the petroleum and chemical industry because of its high energy density [4]. Currently, fossil fuels are the major source of hydrogen production, leading to the formation of greenhouse gases [5]. There are several renewable ways to produce carbon free energies such as biological sources, and electrolysis of water using wind energy and photovoltaic cells [6–9]. Photocatalytic water splitting is one of the most encouraging and alternative ways to generate hydrogen fuel using solar energy as the driving force, which could minimize all probable environmental impacts [10–15]. Till now numerous research articles have been published on renewable hydrogen generation and interesting characteristics of several photocatalytic materials are also reported [16–18].

Strontium titanate ($SrTiO_3$) is one of the most promising and widely studied materials for several applications for the past few decades. $SrTiO_3$ is a semiconductor ceramic material having a simple cubic perovskite structure [19], and can be synthesized by several strategies viz., solid-state, sol-gel, hydrothermal, precipitation, molten salt technique, etc [20–23]. $SrTiO_3$ is a promising candidate for photocatalytic activity especially for hydrogen generation by water splitting [24–26]. Initially, TiO_2 was introduced for solar water splitting and later $SrTiO_3$-based catalytic systems have been widely studied [27–34]. $SrTiO_3$ has characteristics of high thermal and chemical stability and conduction band edge lowered by 200 mV when compared to that of TiO_2. In addition, the indirect bandgap of 3.2 eV reported for $SrTiO_3$ demonstrates its photocatalytic activity in UV region ($\lambda < 387.5$ nm) [35]. Currently, the photocatalytic efficiency of $SrTiO_3$ is tuned by means of various fundamental approaches such as metal ion doping [36,37], facet exposing [38], and co-catalyst loading [39], which are still hot topics.

Thus, the main focus of this review is to support the demand for

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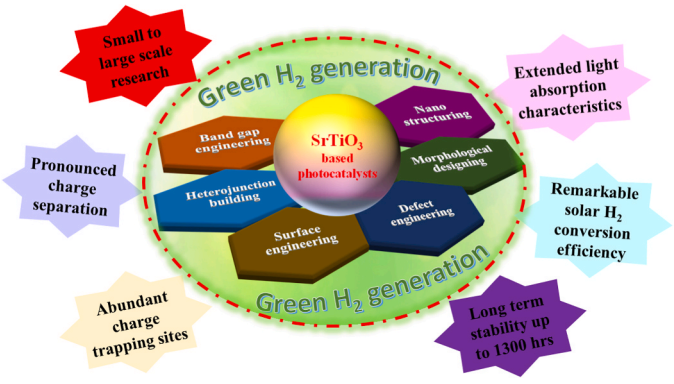
$SrTiO_3$ in the field of solar water splitting. We have highlighted various aspects relating to $SrTiO_3$ such as historical background of water splitting research, crystal structure of $SrTiO_3$, other properties and thermodynamic aspects (Scheme 1). Besides, we have discussed the developments of $SrTiO_3$ by several modification strategies for pronounced photocatalytic hydrogen generation. The fundamental studies including the mechanism for hydrogen generation by $SrTiO_3$ and thermodynamics are explained. Based on the above considerations, interesting facts on $SrTiO_3$-based photocatalysts for water splitting are elaborated. Moreover, this review highlights the mechanism of photocatalysis by $SrTiO_3$-based materials and it is proposed to have efficient photocatalytic systems with the support of an efficient photoreactor for enhanced of hydrogen evolution. The combined and intact information of $SrTiO_3$-based photocatalysts for water splitting will be helpful to the upcoming researchers and specialists to contribute towards this fascinating research field.

2. Historical background of the $SrTiO_3$ based photocatalysts

The research using $SrTiO_3$-based photocatalysts for water electrolysis commenced in 1970 with the Honda-Fujishima effect [40–42]. Earlier, n-type $SrTiO_3$ single crystals were treated as photoanodes in NaOH, KOH, CsOH, or Cs_2CO_3 electrolyte solutions for water splitting reaction [40,41]. In this work, the authors claimed that electrons and holes are generated in $SrTiO_3$ single crystals upon UV light irradiation. Photogenerated holes migrated to the semiconductor/electrolyte interface and reacted with OH^- ions leading to oxygen evolution at the surface of $SrTiO_3$. Similarly, the photogenerated electrons migrated to the anode (e.g., Pt) contribute towards hydrogen evolution by reduction of water. In 1980, $SrTiO_3$ loaded with NiO was reported as an efficient photocatalytic system under UV light irradiation for water splitting [43]. In addition, the efficiency of $SrTiO_3$-based photocatalysts was modified through surface modification, morphological control, and doping. Reaction conditions were also tuned during water splitting for practical applications. In 2018, Goto et al. reported a 0.4% solar-to-hydrogen energy conversion efficiency of $SrTiO_3$ photocatalyst-assisted water splitting, boosted towards commercialization [44].

Fig. 1 shows a schematic of the number of publications for the past 25 years relating to $SrTiO_3$ photocatalytic applications, especially for water splitting and hydrogen energy research. The statistics show that the related publications are increasing day by day and suddenly boosted after 2012. A huge number of papers have been published from 2017 to 2022 though we have lost almost 1 year due to the pandemic COVID 19. These statistic data indicate the importance and demand of $SrTiO_3$-based materials for relevant applications in modern science. Although the number of publications with $SrTiO_3$ material is high enough, limited review articles are available based on its photocatalytic water splitting and hydrogen generation.



Scheme 1. The graphical presentation of the aim and scope of the current review.

3. Crystal structure and properties of $SrTiO_3$

Fig. 2**a** (left) shows the ideal cubic structure of $SrTiO_3$ (space group $Pm\bar{3}m$) at room temperature with lattice parameter $a = 0.3905$ nm [45]. The structural backbone of $SrTiO_3$ is formed by a tightly bound network of octahedral corner shared TiO_6 units which makes it highly stable [46]. Thus, $SrTiO_3$ has a high melting point at about 2080 °C, is eligible for high-temperature modern applications. This characteristic is due to the strong ionic bonding between the strontium and titanium atoms, which requires a large amount of energy to break apart. The crystal structure of $SrTiO_3$ is cubic, meaning that its unit cell has a regular, repeating pattern in all three dimensions. However, under certain conditions such as temperature changes or external stress, the ideal cubic lattice of $SrTiO_3$ can undergo distortions. The most significant types of distortions that occur in $SrTiO_3$ are ferroelectric-type displacement and antiferrodistortive rotation. Ferroelectric-type displacement refers to a shift in the position of the oxygen atoms relative to the titanium atoms in the crystal lattice, resulting in a dipole moment that can be reversed by an external electric field. Antiferrodistortive rotation, on the other hand, involves the rotation of adjacent octahedra in opposite directions, causing a change in the overall symmetry of the crystal structure.

Usually, $SrTiO_3$ shows the cubic structure at room temperature and ambient pressure conditions. Bulk $SrTiO_3$ experiences a cubic-to-tetragonal ($P4mm$) phase transition at about 100–110 K [47,48]. Fig. 2**a** (right) shows the crystal structure of the tetragonal ($Sr_4Ti_4O_{12}$) phase $SrTiO_3$ and surface structure models on $SrTiO_3$ (110) is shown in Figs. 2**b** and 2**c**. The increasing demand of $SrTiO_3$-based materials revealed in Fig. 1 is due to their broad range of unique properties, especially high thermal and chemical stability, large dielectric constant, low dielectric loss, optical and ferroelectric properties [49–51]. Due to its interesting properties, $SrTiO_3$ has a huge number of applications such as memory devices, [52] electro-optical devices [53], sensors actuators [54], and multilayer capacitors [55]. It is frequently used as substrates for epitaxial growth of high temperature superconductors [56,57], and is a conventional nonpolar band insulator which shows a metallic phase with different oxygen non-stoichiometry [58]. Under ambient conditions, $SrTiO_3$ behaves as an electronic insulator and introducing point defects to it can enhance free charge into its lattice.

4. Basic principles of solar water splitting

Photocatalytic solar water splitting is one of the crucial ways for the storage and conversion of solar energy to chemical energy, hence solving the future energy crisis. The current methodology was developed a few decades ago and till now a large number of new insights have been reported. The basic principle of solar water splitting is shown in Fig. 3**a** as presented previously [60–65]. Valence band (VB) electrons of semiconductors travel to the conduction band (CB) upon light irradiation with appropriate wavelengths and leave holes in VB (Fig. 3**a**). Then photogenerated electrons and holes transfer to the photocatalytic surface to contribute towards hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively. In these reactions, the Gibbs free energy change (ΔG) is positive (237.3 kJ/mol) under standard temperature and pressure conditions, demonstrating an uphill and nonspontaneous reaction process (Fig. 3**b**) [61,66]. HER (Eq. 1) and OER (Eq. 2) reactions contribute to overall water splitting reaction while ΔG and the standard redox potential ΔE^0 of the multi-electron water splitting are highlighted below:

$$2H^+ + 2e^- \rightarrow H_2(g) \Delta E^0 = -0.41V \quad (1)$$

$$2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+ + 4e^- \Delta E^0 = +0.82V \quad (2)$$

$$2H_2O(l) \rightarrow H_2\ (g) + \tfrac{1}{2}\ O_2(g)$$

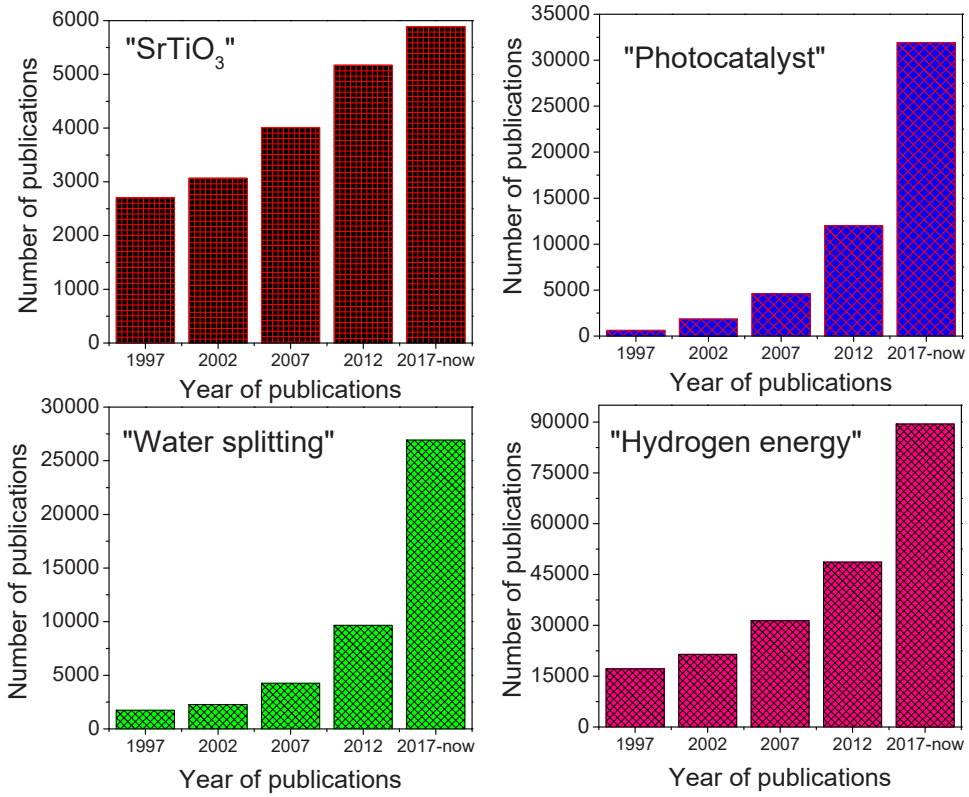


Fig. 1. Number of publications in every five years including open access using "$SrTiO_3$", "Photocatalyst", "Water splitting", and "Hydrogen energy" as the keywords for the past 25 years (Adapted from ISI Web of Science).

$$\Delta G^0 = +237.3 kJ/mol \Delta E^0 = +1.23V \quad (3)$$

Generally, solar water splitting can be performed with powder photocatalyst (Fig. 3**b**) by adopting the photoelectrochemical (PEC) method using photoelectrodes. Semiconductor powder photocatalysts can be dispersed in a water pool under sunlight to generate gas as a consequence of water splitting. Thus, powder photocatalyst systems have the advantage towards large-scale commercial gas production. However, the separation of the generated gas mixture is the main challenge. So, it is mandatory to fabricate an effective photocatalyst for commercial applications.

Due to the limitation of powder photocatalytic systems, the development of PEC cells has been studied for water splitting [60,67–69]. The separation of produced gases is easy in this process but still, the major drawback is the unavailability of appropriate photoelectrode materials with suitable band structure, high stability and large-scale production.

5. Design and development of modified $SrTiO_3$ for water splitting

Scientists have given attention to $SrTiO_3$ owing to its low cost, outstanding chemical stability and promising renewable energy application for photocatalytic water splitting [61,70–74]. It is known that only a minor portion of solar energy belongs to UV region ($\lambda < 400$ nm). Thus, the bandgap of semiconductor photocatalysts should be narrowed for operation under visible light irradiation. When photocatalytic reactions take place, only 5% of UV from sunlight can be utilized due to the wide bandgap of $SrTiO_3$ (3.25 eV). The band structure of $SrTiO_3$ is suitable for this redox reaction of H_2O decomposition. However, $SrTiO_3$ alone cannot perform this reaction due to fast recombination of photogenerated charge carriers. Thus, modification of $SrTiO_3$-based photocatalysts is crucial for water splitting at an advanced level. Recently, ($SrTiO_3$:Al) photocatalyst was tested and reported efficient for overall water splitting with up to 96% external quantum efficiency (QE) under UV light irradiation [16]. Hence, further effort is necessary to develop an optimized $SrTiO_3$-based photocatalyst for commercial applications. The summary of recent reports on $SrTiO_3$ based materials, their synthesis method, the rate of hydrogen generation and quantum efficiencies are given in Table 1. Further, the research on modified $SrTiO_3$ and their activities as low-cost, durable, nontoxic active commercial photocatalysts for water splitting are discussed in detail in this section.

5.1. Bandgap engineering

Bandgap engineering is one of the possible easiest ways to tune the bandgap of semiconductors to get suitable photocatalysts. Thus, a wide number of reports are available for fine-tuning band gap of $SrTiO_3$ to stimulate visible-light absorption including metal doping[75,96], nonmetal doping [97], or doping with other relevant elements [77,98, 99]. However, the reduction in bandgap cannot always enhance the efficiency of the photocatalysts because it is also depending on the position of VB and CB edges [100]. For proton reduction, CB and VB should reach a potential lower than 0 V (vs. NHE (H^+/H_2)) and 1.23 V, respectively. The band structure of $SrTiO_3$ and corresponding redox potentials of doped materials for water splitting is shown in Fig. 4**a**. The introduction of 3d-transition metals in $SrTiO_3$ leads to localized states within its band gap region, which is a major disadvantage in photocatalysis. Therefore, the implementation of transition metal alone as a dopant in $SrTiO_3$ is not appropriate for enhanced photocatalytic activity. In the case of nonmetal doping, the band gap of $SrTiO_3$ can also be reduced while the localized states appear deep inside the forbidden region. This may result in trapping photoexcited charge carriers and increase the electron–hole recombination rate which reduces photocatalytic activity efficiency [96]. Thus, co-doping is considered an efficient strategy for creating a continuum band in the forbidden region in dopants, thereby stabilizing the entire catalytic system [101]. In this

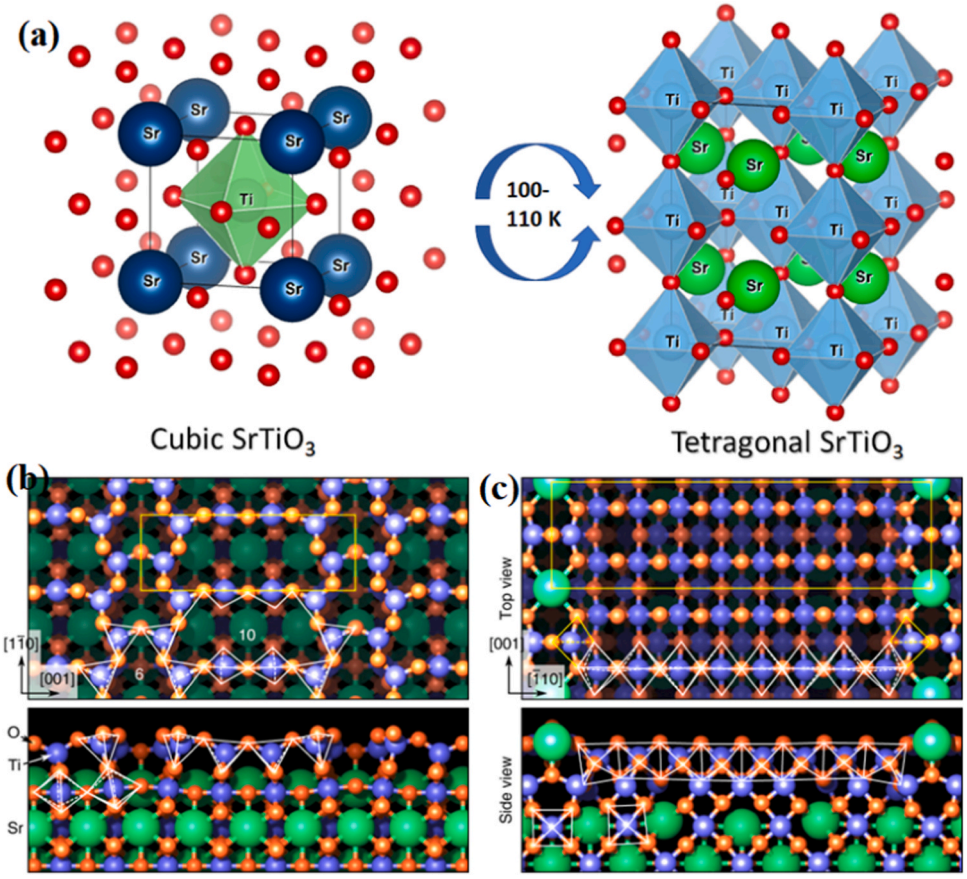


Fig. 2. (a) Crystal structure of cubic (left) and tetragonal $SrTiO_3$ (right). **(b)** $SrTiO_3$ (110)–(4 × 1) surface reconstruction consists of 10 and 6-membered rings of corner-sharing tetrahedra and (c) $SrTiO_3$ (110)–(2 × 5) surface reconstruction consists of a bilayer of octahedra. Reprinted with permission, copyright, 2018, Springer Nature [59].

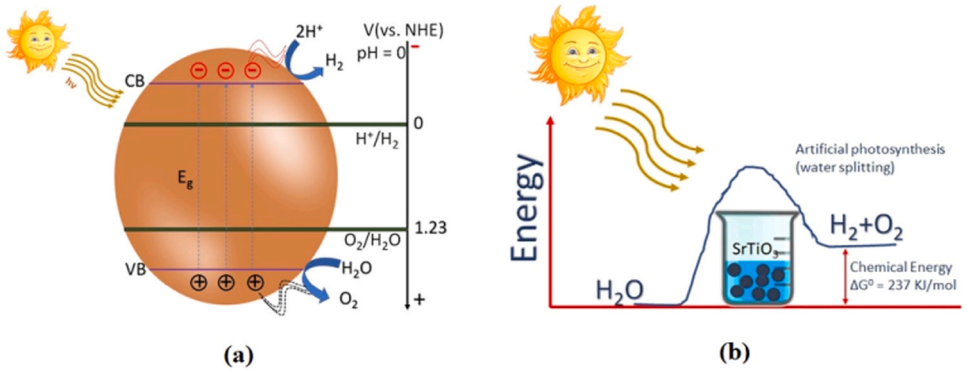


Fig. 3. (a) Schematic diagram of the basics of the overall solar water splitting in semiconductor photocatalysts. **(b)** Thermodynamically uphill reaction process of photocatalytic solar water splitting.

way, band engineering can be accomplished to make the spectral response in the visible region with better photocatalytic performance [102]. Quan et al., reported the band engineering of $SrTiO_3$ with $Zn_xCd_{1-x}S$ nanoparticles to a three-dimensionally ordered microporous structure for efficient hydrogen generation [78]. The corresponding band structures describing the enhanced charge transfer process is as shown in Fig. 4**b**. The estimated bandgaps of 3D-$SrTiO_3$ and $Zn_{0.5}Cd_{0.5}S$ are 3.27 eV and 2.20 eV, respectively, and the determined VB potentials are 2.78 V and 1.63 V (vs. NHE), respectively.

5.2. Heterojunction building

Finding optimum semiconductors is one of the main issues to develop PEC water splitting devices. These materials play an important role to determine the number of photoexcited carriers involved in solar water splitting [104]. The construction of an ideal heterojunction for a specific material leads to PEC water splitting enhancement by endorsing charge separation process and stability under photoexcitation [105–108]. The optimized heterojunction construction of $SrTiO_3$ and other materials is crucial to increase the absorption of solar light and promote charge separation [109]. The working procedure of different types of oxide-based heterojunctions has already been discussed in detail [110].

Table 1
Comparison of various strategies adopted for enhancing the photocatalytic performance of some of the reported $SrTiO_3$ based catalytic systems.

Catalytic system	Synthesis method	Strategies	Key parameters	Hydrogen production rate	Quantum efficiency	Ref.
Cr-doped $SrTiO_3$, with Pt (0.6 wt%) as a cocatalyst	Sol–gel hydrothermal route	Doping with transition metals	Band gap reduction	82.6 mmol h^{-1} in 20% methanol solution	2.95% at 410 nm	[75]
La,Cr-codoped $SrTiO_3$	Sol−gel hydrothermal process	Doping with lanthanide series	Band gap reduction	326.8 μmol h^{-1} in CH_3OH aqueous solution containing 5 M NaOH	25.6% at 425 ± 12 nm	[76]
Cr/Ta co-doped $SrTiO_3$	Polymerizable complex (PC) method	Co-doping	Band gap reduction	122.6 mol h^{-1}	2.6% at 420 nm	[77]
3D $SrTiO_3$ decorated with $Zn_xCd_{1-x}S$ with 1.5 wt% Pt as co-catalyst	Colloidal crystal template method followed by chemical co-precipitation method	Surface decoration	Charge transfer efficiency	19.67 mmol g^{-1} h^{-1} in deionized water containing Na_2SO_3 (0.1 mol L^{-1}) and Na_2S (0.1 Mol L^{-1})	35.9% at 420 nm	[78]
TiO_2/ $SrTiO_3$ @g-C_3N_4	Hydrothermal synthesis followed by chemical bath deposition technique	Band gap engineering/ Heterojunction building	Charge transfer efficiency	73 μmol/cm^2	-	[79]
N doped Graphene Quantum Dots/ $SrTiO_3$(Al)/CoO_x	Hydrothermal method	Band gap engineering/ Heterojunction building	Charge transfer efficiency	18.8 μmol h^{-1}	-	[80]
Surface reconstructed $SrTiO_3$	Thermal treatment	Band gap/ Surface engineering	Charge transfer efficiency	202.8 mmol h^{-1}	-	[81]
$SrTiO_3$	Rapid laser-melting method	Defect engineering	Band gap reduction	2.46 μmol/ (h g)		[82]
Prevoskite $SrTiO_3$	Hydrothermal	Defect engineering	Oxygen vacancies	2.2 mmol h^{-1} g^{-1}	-	[83]
MoO_y/$RhCrO_x$/STO:A	Flux method followed by photodeposition	Defect engineering	Charge transfer efficiency	4.6 mmol h^{-1}	69% at 365 nm	[84]
$SrCl_2$ flux treated $SrTiO_3$/ cocatalyst loaded $Rh_2-yCr_yO_3$	Mechanical grinding followed by calcination, and cocatalyst loading by impregnation method	Defect engineering	Crystallinity and charge transfer efficiency	550 μmol h^{-1}	30% at 360 nm	[85]
2% Al^{3+}-doped $SrTiO_3$	Polymerizable complexation method	Defect engineering	Oxygen vacancy and charge transfer efficiency	1.256 mmol h^{-1}	55.46% at 365 nm	[86]
$SrTiO_3$/TiO_2 NP	Hydrothermal method	Morphology control	Rapid charge transfer	0.731 mmol	-	[87]
$SrTiO_3$ nanofibers	Electrospinning method followed by calcination	Morphology control	Rapid charge transfer	330 μmol h^{-1} g^{-1}	0.70% at 365 nm	[88]
La,Al-codoped $SrTiO_3$	Flux treatment method	Surface/defect engineering	Oxygen vacancies	1.79 mmol h^{-1}	78.43% under 365 nm	[89]
$SrTiO_3$-TiO_2	Hydrothermal method	Heterojunction engineering	Rapid charge transfer	10.6 μmol h^{-1}	8.6% at 365 nm	[90]
La- and Rh-co-doped $SrTiO_3$ (STO:La/Rh)	Hydrothermal Method	Surface/defect engineering	Charge transfer efficiency	48 μmol h^{-1}	-	[91]
TiO_2/CoOOH/$RhCrO_x$/ $SrTiO_3$	Flux method followed by photodeposition	Material designing for extended light absorption	Long-term durability	~ 36 mmol h^{-1}	> 50% at 365 nm	[92]
Ru/$SrTiO_3$/TiO_2	Electrospinning followed by hydrothermal and electrophoresis	Defect engineering	Interfacial charge separation	0.99 mmol g^{-1} h^{-1}	> 20% at 365 nm	[93]
Ni_2P Engineered $SrTiO_3$ Nanocubes	Electroless plating	Surface engineering	Bandgap	7.03 mmol g^{-1} h^{-1}	23.72% at 400 nm	[94]
$SrTiO_3$-T/$Cd_{0.5}Zn_{0.5}S$	Hydrothermal method	Defect engineering	Oxygen vacancy	25.01 mmol g^{-1} h^{-1}	-	[95]

Several recent reports claimed $SrTiO_3$ based heterojunctions as highly efficient photocatalytic systems such as Sb:SnO_2 @TiO_2–$SrTiO_3$ [107, 111]. Another optimized $SrTiO_3$-based heterojunction reported is TiO_2/$SrTiO_3$ @g-C_3N_4 claimed as type II heterojunction (Fig. 4**c**) [79]. TiO_2 is a semiconductor with less negative VB and CB compared with $SrTiO_3$. Therefore, it is a suitable match for the band edges between TiO_2 and $SrTiO_3$ contributing to a type II heterojunction. Thus, the photogenerated electrons of $SrTiO_3$ from its CB is transferred to the CB of TiO_2, and the photogenerated holes are transferred from the VB of TiO_2 to that of $SrTiO_3$. However, the VB and CB of g-C_3N_4 are more negative than those of TiO_2, hence the fast transfer of photogenerated electrons from VB of g-C_3N_4 to CB of TiO_2 is accomplished, thereby leaving photogenerated holes at the VB of g-C_3N_4. This complex increases the spatial separation of photogenerated charge carriers in $SrTiO_3$/TiO_2/g-C_3N_4 system which reduces the probability of recombination.

5.3. Surface engineering

In modern science, surface engineering of $SrTiO_3$-based materials is widely used to improve water-splitting activity. Widely studied semiconductor materials (viz., TiO_2, SnO_2, Fe_2O_3, WO_3, etc.) were modified via various surface engineering techniques to improve their catalytic activities and functionalities [112–116]. Various surface engineering strategies reported for enhancing the photocatalytic performance are cocatalyst loading techniques [117,118], and modification by organic dyes [119], plasmonic materials [120,121], or quantum dots (QDs) [122]. Wang et al. reported the photocatalytic activities of variously shaped $SrTiO_3$ **(**Fig. 5**a-d)** obtained after hydrogenation at 350 °C for 60 min [123]. Their performance towards photocatalytic hydrogen generation was tuned by surface engineering and consequently, revealed a greater hydrogen generation rate than pristine ones (Fig. 5**e**). The significant increase in photocatalytic hydrogen generation activities is ascribed to the enhanced charge transfer characteristics owing to the generated oxygen vacancies generated within the disordered overlayer.

Besides, surface decoration of $SrTiO_3$ with QDs was also attempted further to enhance its PEC water splitting performance [81,124–127]. Among the numerous ways, porous and solid $SrTiO_3$ films were developed and carbon QDs were used as the functional modifiers to decorate the $SrTiO_3$ surface [124]. They claimed superior electron-hole transfer and separation rates for $SrTiO_3$-CDs through the interface and high PEC

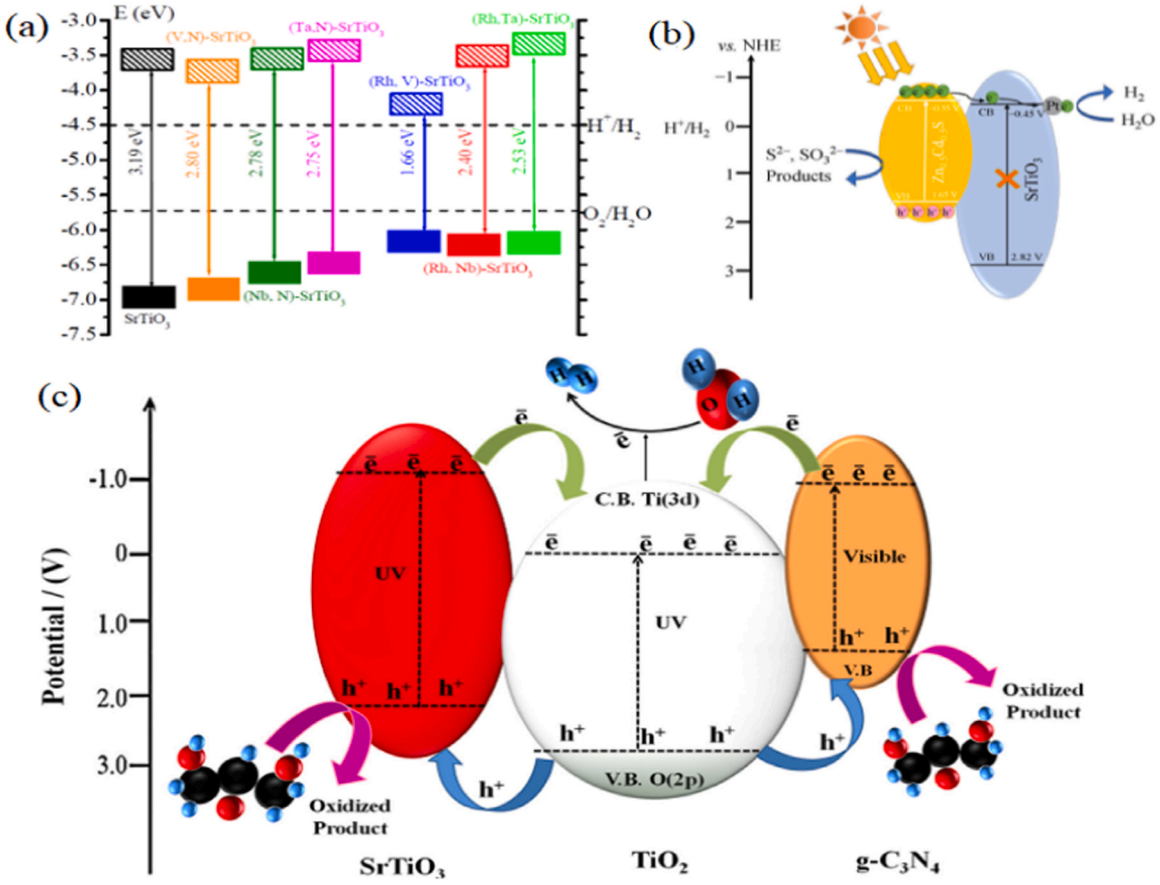


Fig. 4. **(a)** Band edge positions of $SrTiO_3$ and doped semiconductors corresponding to water reduction and oxidation potential levels of H^+/H_2 and O_2/H_2O, respectively [78]. **(b)** Schematic representation of band structures and charge transfer pathways of the $SrTiO_3$ decorated with $Zn_xCd_{1-x}S$ composite photocatalysts. Reprinted with permission, copyright, 2021, Springer Nature [103]. **(c)** Schematic demonstrating the separation of charge carriers in $TiO_2/SrTiO_3$ @g-C_3N_4 nanorod heterostructure. Reprinted with permission, copyright, 2018, Elsevier [79].

performance. Sreedhar et al. showed enhanced PEC water splitting performance of CdSe quantum dot sensitized $SrTiO_3$ and obtained a higher current density, which is twice of that of the bare one [127]. Recently, Liu et al. prepared N-doped graphene QDs cocatalysts along with $SrTiO_3$(Al)/CoO_x photocatalysts for hydrogen evolution by water splitting [80]. $SrTiO_3$(Al) and $CoO_x/SrTiO_3$(Al) showed low photocatalytic overall water splitting activities. After surface engineering using N-doped graphene QDs, its activities were significantly enhanced (nearly 4 times, Figs. 5**f** and 5**g**). As proposed in the working mechanism of engineered $SrTiO_3$(Al) surface for photocatalytic water splitting (Fig. 5**h**), VB electrons of $SrTiO_3$(Al) travel to CB of N-doped graphene QDs through Ti–O–C chemical bonds under sunlight excitation. The reticent electrons in N-doped graphene QDs contribute to hydrogen evolution at the surface-active sites of pyrrole N species.

5.4. Defect engineering

Defect engineering has an important role in bandgap manipulation by creating point defects in $SrTiO_3$ through cationic and anionic vacancies [82,128]. For example, the fabricated crystalline core/amorphous $SrTiO_3$ @$SrTiO_{3-x}$ by the creation of 3.28% (atom) of oxygen vacancy concentration showed 2.3 times higher hydrogen evolution rate than pure $SrTiO_3$ under sunlight [83]. Ti^{3+} and oxygen vacancies were inserted into $SrTiO_3$ by establishing Ruddlesden–Popper using the preparation of self-doped $SrTiO_{3-\delta}$ adopting a carbon-free one-step combustion strategy that leads to the formation of the narrow band gap, improved visible light absorption and photocatalytic performance [129]. In general, oxygen vacancies play a significant role to augment photocatalytic activity. There are two types of oxygen vacancies, i.e., surface oxygen and bulk oxygen vacancies within the bulk materials [130]. Surface oxygen vacancies of $SrTiO_3$ serve both as charge trapping cites and as adsorption sites which helps to prevent the recombination of photogenerated charge carriers, but only charge traps were noticed in bulk oxygen vacancies which resulted in lower photocatalytic performance [131].

Typically, $SrTiO_3$ shows two types of defects that are oxygen vacancies and Ti^{3+} which create a fence of better catalytic performance [132]. Doping with Li^+, Na^+, Rh^+, Mg^{2+}, Al^{3+}, Ga^{3+}, and In^{3+}, which are low valence cations, gradually enhanced overall photocatalytic performance due to Ti^{3+} defects by becoming an n-type semiconductor [37,84]. Domen et al. found a relatively better photocatalytic activity in Al^{3+} doped $SrTiO_3$ that reached 30% apparent quantum efficiency (AQE) by loading $Rh_{2-y}Cr_yO_3$ co-catalyst [85]. Further, they increased the AQE by nearly 100% at 360 nm by selecting photo-deposition of Rh/Cr_2O_3 and CoOOH co-catalysts on anisotropic crystal facets [16]. Recently, Su et al. reported the synergism between oxygen defects at the surface and that of bulk Ti^{3+} on $SrTiO_3$ towards augmenting the overall photocatalytic performance [86]. Fig. 6 shows the water splitting activities and schematic of charge transfer and mechanism of defect formation in $SrTiO_3$-based photocatalysts.

5.5. Nanostructure construction and morphology control

Various approaches have been performed to expose the drawbacks of bulk $SrTiO_3$. Conventionally, $SrTiO_3$ can be synthesized using $SrCO_3$ and TiO_2 precursor through a solid-state process. Nanostructured $SrTiO_3$

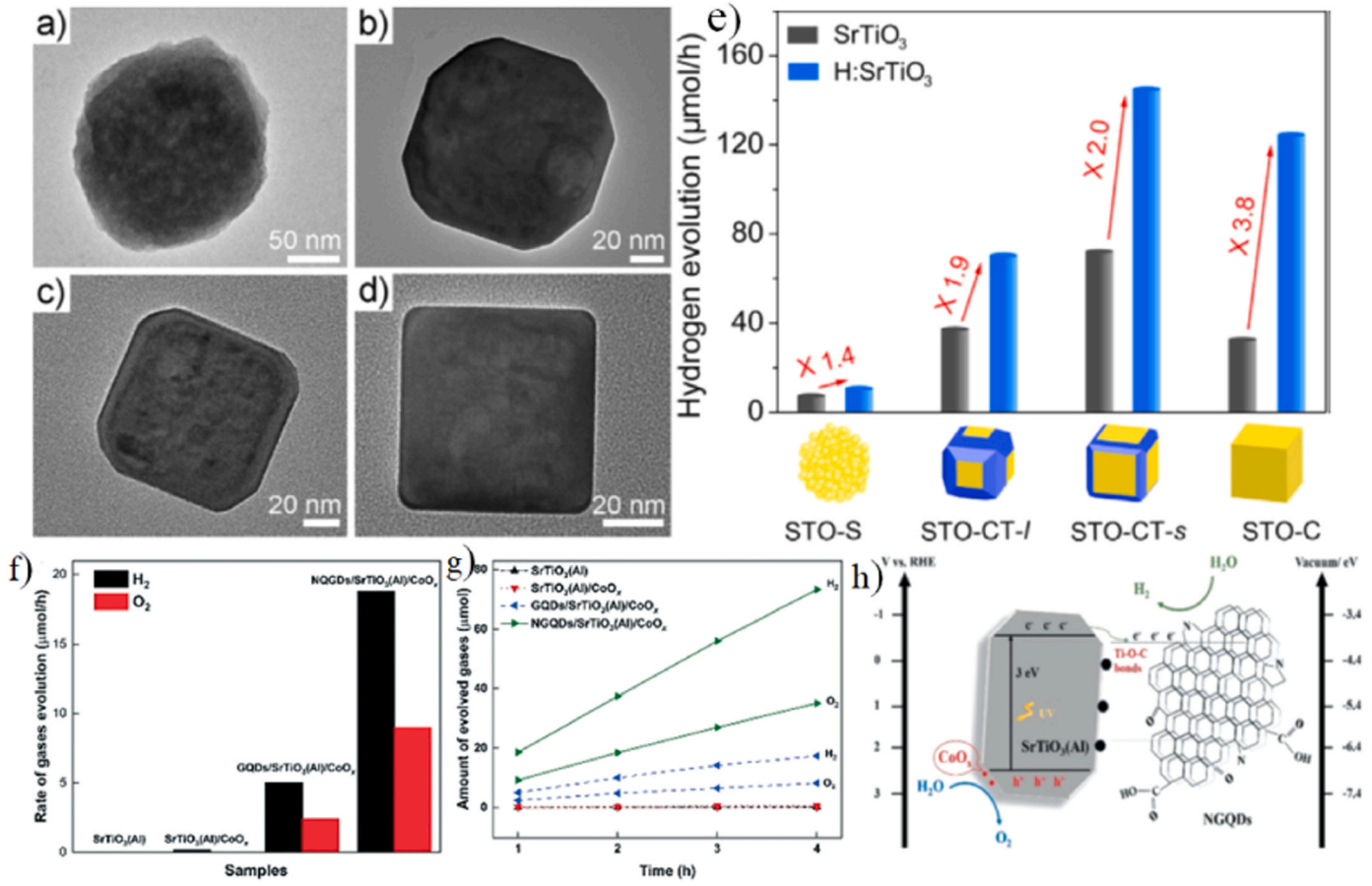


Fig. 5. HRTEM images **(a)** H: $SrTiO_3$-S, **(b)** H: $SrTiO_3$-CT-/, **(c)** H: $SrTiO_3$-CT-s **(d)** H: $SrTiO_3$-C viewed from [001] direction. **(e)** Photocatalytic hydrogen production rate over various hydrogenated $SrTiO_3$ with different morphologies vs. the pristine one. Reprinted with permission, copyright, 2016, John Wiley and Sons [123]. **(f)** Overall rate, **(g)** time course profiles, and **(h)** schematic of the proposed mechanism for photocatalytic water splitting with NGQDs/$SrTiO_3$(Al)/CoOx photocatalyst. Reprinted with permission, copyright, 2021, Springer Nature [80].

with decreased particle size and high surface area reduces diffusion length for the photogenerated electron-hole pairs to reach surface-active sites and consequently, the recombination rate will be reduced. This improves the charge carrier collection favoring an enhanced PEC water splitting [87,133]. However, morphological designing of $SrTiO_3$ can improve the light absorption ability and charge separation efficiency. Various strategies have been further developed to increase the light absorption ability of $SrTiO_3$-based photocatalytic systems by: **(1)** fabricating a specific morphology through a complex structure [134], **(2)** reduction of the particle size [135], **(3)** construction a heterostructure [136], and **(4)** engineering to expose active sites [137]. Therefore, the development of modern $SrTiO_3$-based photocatalysts with micro–nanostructures would be an advantage. Nanostructured $SrTiO_3$ with different morphologies (e.g., nanoparticles, nanotubes, nanoplatelets, etc.) was already reported as efficient materials for PEC water splitting. Recently, Kong et al. reported the synthesis of different $SrTiO_3$ morphological structures for photoelectrochemical cathodic protection. Literature reports confirm the predominant role of organic molecules (viz., polyvinyl alcohol, polyvinylpyrrolidone and ethylene glycol) in morphology regulation of $SrTiO_3$ that can control the evolution and crystallization of crystal surface [138]. Recently reported different micro-morphologies of the prepared $SrTiO_3$ samples are shown in Fig. 7. Recently, Hu et al. reported a notable advancement in the field of photocatalysis with their investigation of the superior photocatalytic efficiency observed in 1D CF/$SrTiO_3$/CdS core–shell structures for hydrogen generation [139]. The incorporation of CdS nanospheres resulted in an extension of the light absorption capacity into the visible spectrum, an enhancement of charge separation efficiency, and a facilitation of rapid migration of photogenerated charge carriers. Fang et al. conducted an exploration into the potential of a designed TiO_2/$SrTiO_3$ core–shell heterojunction as a viable component in low-temperature, high-performance ceramic fuel cells [140].

Furthermore, a series of core@shell $SrTiO_3$ @NiFe LDH nanosystems demonstrated remarkable performance in the realm of photocatalytic activities [142]. This outcome was attributed to the broadening of absorption spectra, effective charge transport, and suppression of recombination events among photogenerated charge carriers. The polyhedral morphologies in $SrTiO_3$ have been shown anisotropic charge transfer properties that prove advantageous for enhancing light absorption capabilities [143–145]. Furthermore, nanostructured photocatalytic concepts have engendered considerable attention, due to their high active surface areas, abundance of reactive sites, and noticeable migration of charge carriers that are essential for applications involving water splitting. The nanosheet configurations of Copper (Cu^0/Cu^{2+}) modified $SrTiO_3$ have exhibited notable efficiency in the photocatalytic HER and CO_2 reduction [146]. This success can be attributed to the efficient separation of photogenerated charge carriers facilitated by Schottky contacts. An additional noteworthy development is the realization of nano hetero-structural platelets of $SrTiO_3$/$Bi_4Ti_3O_{12}$, as elucidated by Maček Kržmanc et al. [147]. These structures have demonstrated remarkable proficiency in photocatalytic hydrogen generation, notably in the absence of noble metal dopants or cocatalysts. In a novel advancement, an intricate direct Z-scheme photocatalytic tandem system involving Pt-$SrTiO_3$:Rh and $BiVO_4$ has exhibited strong and long term performance in visible light-driven water splitting [148]. This innovative configuration offers deeper insights into a fresh approach for

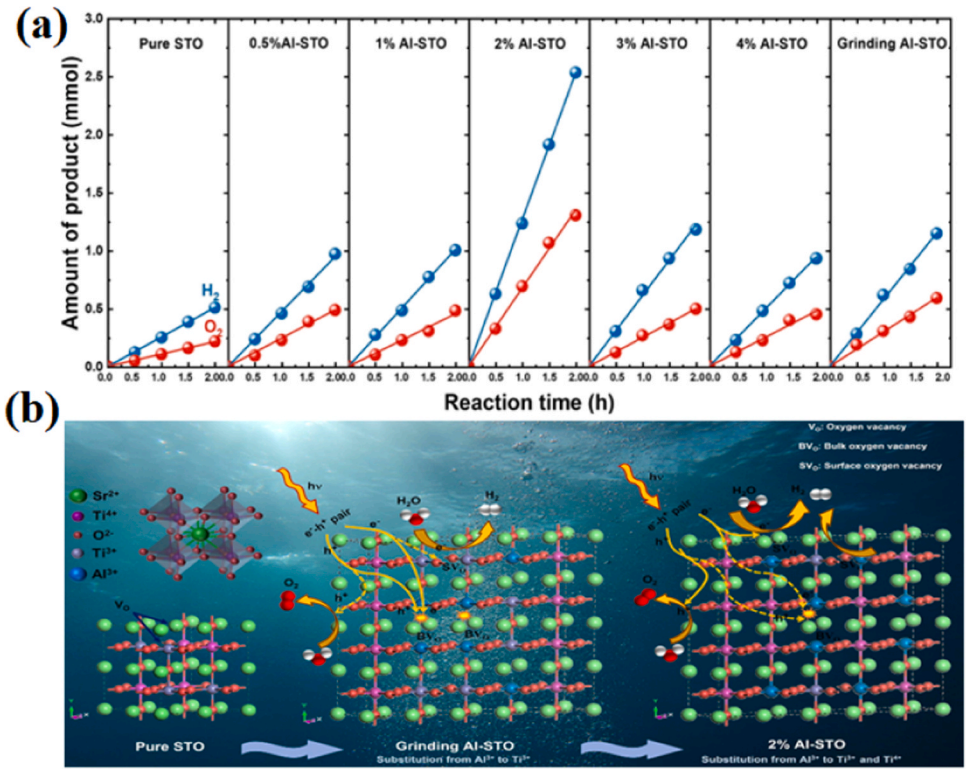


Fig. 6. **(a)** Photocatalytic hydrogen and oxygen evolution rates with $SrTiO_3$-based photocatalysts. **(b)** Scheme corresponding to charge carrier transfer and mechanism corresponding to defects in $SrTiO_3$-based photocatalysts. Reprinted with permission, copyright, 2022, Elsevier [86].

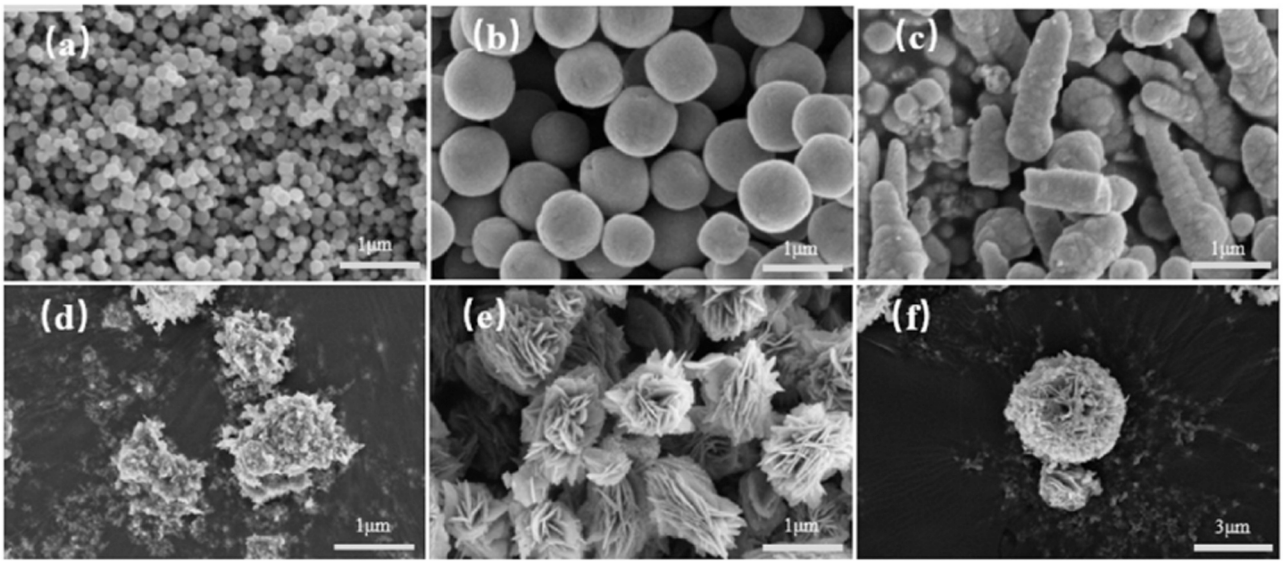


Fig. 7. SEM images of different $SrTiO_3$ systems: **(a)** nanoparticles, **(b)** nanoballs, **(c)** nanorods, **(d)** coral stone-like microspheres, **(e)** small flower-like microspheres, and **(f)** large flower-like microspheres. Reprinted with permission, copyright, 2022, Elsevier [141].

the design and assembly of adept artificial photosynthetic systems dedicated to photocatalytic HER.

5.6. *Influence of sacrificial agents*

Sacrificial agents (SAs) refer to chemical species working in various photocatalytic processes to facilitate electron transfer and influence the efficiency of target reactions, particularly in the context of hydrogen generation [149]. SAs typically encompass a range of substances, including sensitizers, dyes, and metal complexes, which act as intermediaries for electron transfer mediators [150]. In the case of scalable and economically prospects of photocatalytic processes, the choice of sacrificial agents becomes crucial. However, the practical applicability of certain inorganic SAs can prove uneconomical when considering the scalability of the process. Conversely, organic SAs offer a more cost-effective and less toxic alternative, rendering them advantageous for industrial-scale applications. $SrTiO_3$-based photocatalysts have established recognition for their proficiency in Z-scheme water splitting, exemplifying cutting-edge performance levels. Nonetheless, inherent limitations within the $SrTiO_3$ structure including structural

deformities and inefficiency in utilizing the wide light absorption characteristics remain challenges. Consequently, the introduction of sacrificial agents stands as a strategic attempt aimed at modifying these inherent constraints.

In most of the cases, photocatalytic systems based on $SrTiO_3$ are found to be active enough in the presence of SAs. Furuhashi et al., reported the photocatalytic HER capabilities of $SrTiO_3$:Rh within an aqueous medium containing methanol as the sacrificial agent [151]. Notably, this HER activity was found to be absent in pure water. This observation underscores the crucial role of sacrificial agents in enabling and enhancing the photocatalytic performance of $SrTiO_3$-based systems. Moreover, Asai and colleagues expanded their investigation of the $SrTiO_3$:Rh system by adjusting the ratios of Rh/Sb and adding an IrO_2 cocatalyst [152]. These changes led to an enhanced and prolonged photocatalytic performance, emphasizing the complex interaction between composition and catalytic effectiveness. In $SrTiO_3$-based Z-scheme photocatalytic setups, electron transfer usually occurs through interfacial heterojunctions or electron mediators. Various substances have been studied for this purpose, such as Au [153], reduced graphene oxide [154], Ir [155], and carbon-based materials [156]. Each of these materials helps adjust the paths of charge transfer, impacting the overall efficiency of photocatalysis.

6. Recent advances and interesting facts on $SrTiO_3$-based photocatalysts

As discussed in Section 5, tuning the properties of $SrTiO_3$ improves its ability to absorb photons, reducing electron loss during photoexcitation. New designs, including various structures and binary systems, have emerged to make this approach more feasible. For instance, Phoon et al. found that the photocatalytic performance of these systems depends largely on the surface properties and dopant concentration in $SrTiO_3$-based materials [157]. We still need to continue the study to optimize them to augment the passage of charge carriers at the excited state under solar light irradiation. Commercialization of $SrTiO_3$-based materials is of great significance for renewable hydrogen generation in the near future. So, recent interesting facts and progress on $SrTiO_3$-based materials have been discussed in the following sections to accomplish the milestone of photocatalytic hydrogen generation from water splitting.

6.1. Photocatalytic water splitting with a QE of almost unity

As the economic and potential solar hydrogen production by overall water splitting is the current interest, designing narrow bandgap semiconductors with high photocatalytic QE is crucially important for accomplishing enhanced solar energy conversion efficiency. Earlier studies claimed a QE of less than 10% for overall photocatalytic water splitting [62]. In general, solar water splitting is an uphill reaction with complex electron transfer processes. The design of photocatalysts with 100% internal QE is a challenging endeavor if it is not impossible. The recombination rate of photogenerated electron-hole carriers and two-electron injection for HER and four-hole injection for the OER should be considered. Owing to the high possibilities of backward electron transfer, few reports of water splitting with an apparent QE more than 50% have been claimed, even with UV active photocatalytic systems [44,84,158]. This impossible task has been realized due to achieving improved external QE up to 69% from $SrTiO_3$-based photocatalysts over the past years [84,85,159]. Recently, Takata et el. further increased the external QE by developing cocatalysts site-selectively on $SrTiO_3$:Al particles using a stepwise photodeposition method [16]. They claimed the overall water splitting at 96% external QE at 350–360 nm wavelength (Fig. 8**b**), equivalent to an internal QE of almost unity.

The photocatalytic water-splitting of $SrTiO_3$:Al loaded with Rh, Cr and Co species as cocatalysts is shown in Fig. 8**a**. Remarkable photocatalytic performance was reported for 0.05 wt%Cr and Co loading. The external QE values (Fig. 8**b**) were 95.7%, 95.9%, and 91.6% at 350, 360, and 365 nm, respectively, as the maximum values recently reported. The

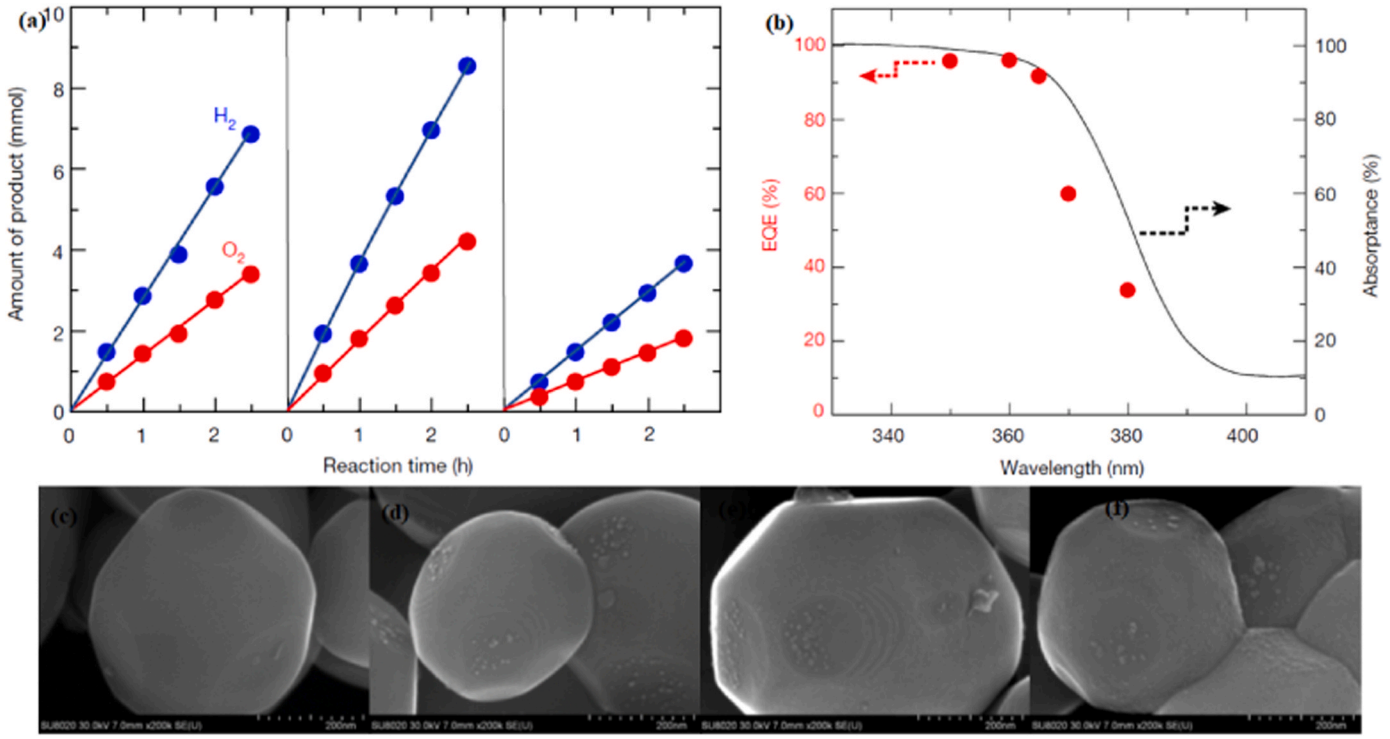


Fig. 8. (**a**) Time course profiles corresponding to hydrogen and oxygen evolutions over $SrTiO_3$:Al loaded with cocatalysts upon light irradiation. (**b**) UV–vis DRS of lone $SrTiO_3$:Al and AQE with Rh(0.1 wt%)/Cr_2O_3(0.05 wt%)/CoOOH(0.05 wt%)-@$SrTiO_3$:Al. (**c–f**) SEM images to show the location of cocatalysts of $SrTiO_3$:Al loaded with various cocatalysts. Reprinted with permission, copyright, 2020, Springer Nature [16].

corresponding SEM images of step-by-step cocatalytic photo-deposition engineering at the nanometer range on $SrTiO_3$:Al-based photocatalysts are shown in Fig. 8(**c-f**). The selective cocatalysts deposition at crystal facets of the photocatalytic particles via anisotropic charge transfer mechanism highly enhanced both HER and OER.

6.2. Atomic-level surface microstructure and plasmon-induced HER

The strong interaction between light and matter at the surface of a catalyst in a plasmonic photocatalytic system offers an exceptional way towards the green solar-to-chemical energy conversion process [160–163]. Among several strategies, interface/surface engineering significantly tunes the activity of plasmon-induced water splitting. This phenomenon inspires engineering of plasmonic heterostructures even at the atomic level. Special types of materials are used in plasmonic photocatalysts viz., Au, Ag, and Cu, which can restrict the free electrons oscillating with external incident radiation. Many attempts on plasmonic metals have been reported by monitoring shapes, particle size and composition to enhance photocatalytic activities by tuning the utilization of hot carriers [164–166]. The interfacial Ti^{4+} between Au and TiO_2 can inject hot electrons due to the tunnelling effect in plasmonic Au/TiO_2 photocatalyst [167]. In the case of $SrTiO_3$ as a ternary oxide system, the surfaces at a microstructural level could be exposed to dissimilar layers of the outer region at atomic levels considering Sr-O layers or TiO_2 layers [168–170]. A similar case was reported by Zeng et al. [120], where Au/$SrTiO_3$ with Ti-terminated and Sr-terminated surfaces was synthesized to gain more insights into surface plasmon resonance induced HER (Fig. 9**a**).

Based on absorption data, comparable plasmon absorption and Au size were found for both Au/$SrTiO_3$ samples with Ti- and Sr-terminated surfaces. However, the HER of the latter was 3 times higher activity (Fig. 9**b**). The introduction of triethanolamine hole as a sacrificial reagent has enhanced HER activity of Au/$SrTiO_3$ with Sr-terminated surfaces (Fig. 9**c**). Photocatalytic HER for Au/$SrTiO_3$ as a function of wavelength is as shown in Fig. 9**d**, which corroborated well with the surface plasmon resonance absorption. The enhancement in HER activity was introduced by the surface plasmon resonance excitation. Further experiments were performed to approve the surface dependency over photocatalytic performance (Fig. 9**e**). This recent interesting work also refers to the variation in Au/$SrTiO_3$ interfaces substantiating the charge separation process. It atomically unravels the surface microstructure dependency on plasmon-induced HER, thereby paving the way for fabricating effectual plasmonic systems for solar-to-chemical energy conversion.

6.3. Consequences of surface engineering on defect engineering and HER

Generally, high temperature treatment of $SrTiO_3$ releases lattice oxygen and the formed oxygen vacancies reduce Ti^{4+} to Ti^{3+}. This problem was solved by defect engineering, i.e., with doping low-valence cations at B-site. Further, this doping via flux method showed outstanding photocatalytic activity towards overall water splitting [85, 171,172]. In $SrTiO_3$, Sr-based suboxide phase is dominant in perovskite surface which has less possibility to create oxygen vacancies when compared with Sr-based oxides in perovskite [83,173,174]. Sr^{3+} in Sr-based suboxide can effectively decrease the concentration of Ti^{3+} in the perovskite lattice. Implementing oxygen vacancies in $SrTiO_3$ increases the equilibrium density of electrons leading to a positive shift in Fermi level, revealing the trend towards p-type semiconductors [88, 175]. The novelty of metal ion doping in $SrTiO_3$ and the influence of Fermi level resonance on water-splitting reaction have been studied recently by Qin et al. [89]. The corresponding SEM images of the proposed $SrTiO_3$ based catalyst and exposure of specific crystal facets are represented in Fig. 10 **(a-i)** [89].

The amount of gas evolved after fine tuning the necessary characteristics of $SrTiO_3$-based catalytic systems is shown in Figs. 10**j** and 10**k**. The reported AQE was enhanced from 28.06% to 78.43% by reducing defects and stabilizing crystal structures. A recently proposed mechanism for defect engineering of lanthanum- and aliovalent-codoped $SrTiO_3$ is illustrated in Fig. 10**l**. Generally, Ti–O bond dissociates and forms oxygen vacancies. The doping of Al^{3+} converts Ti^{3+} to Ti^{4+}, which could enhance photocatalytic HER. Further Al^{3+} doping of Sr^{2+} via lattice shrinkage is done on perovskite structures. Again, La^{3+} promotes Sr^{2+} ions at the surface going into the perovskite owing to structural distortion. Furthermore, by introducing structural and chemical defects, functional degrees of freedom can be extended. These defects usually occur together, and the requisite characteristics can be effectively tuned. Recent work relating to the same provides meaningful guidance for designing such $SrTiO_3$-based photocatalysts in near future.

6.4. Design of unique complex multishelled structured photocatalysts

Harvesting of incident light has a crucial role for improving solar energy conversion efficiency that depends on two factors: (i) the

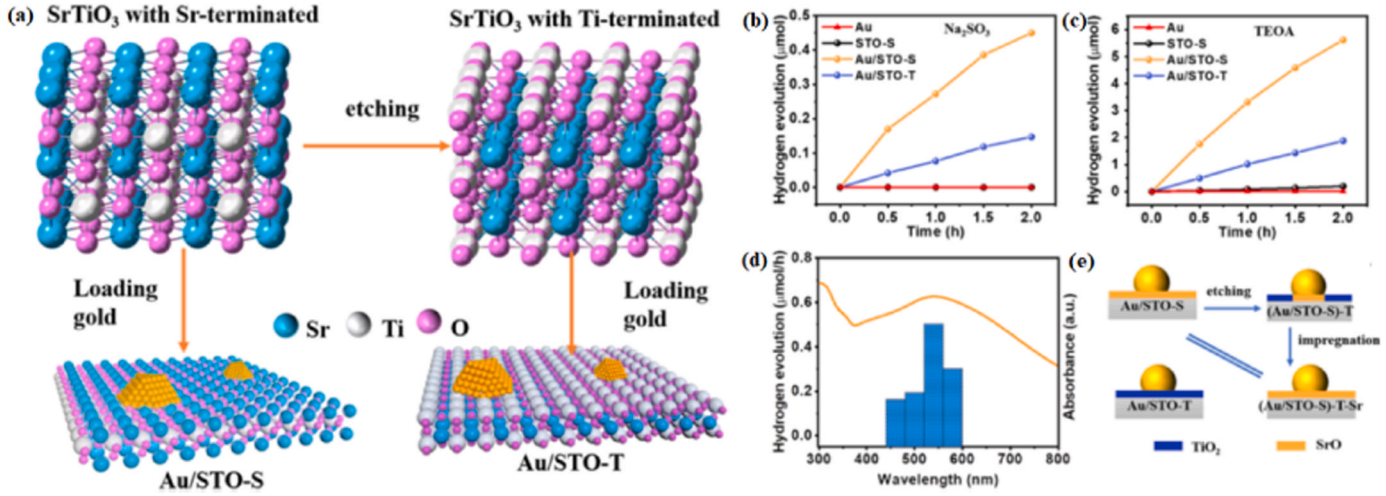


Fig. 9. (**a**) Schematic of Au/$SrTiO_3$ heterostructures. Photocatalytic HER performance of Au, Sr-terminate surface, Au/$SrTiO_3$ with Sr-terminate surface and Au/$SrTiO_3$ with Ti-terminate surface in the presence of (**b**) Na_2SO_3 and (**c**) triethanolamine hole sacrificial reagent. (**d**) Plasmon absorption spectrum and photocatalytic activity of Au/$SrTiO_3$ with Sr towards HER. (**e**) Schematic of Au/$SrTiO_3$ with Sr-terminate surface and Au/$SrTiO_3$ with Ti-terminate surface heterostructures. Reprinted with permission, copyright, 2022, Elsevier[120].

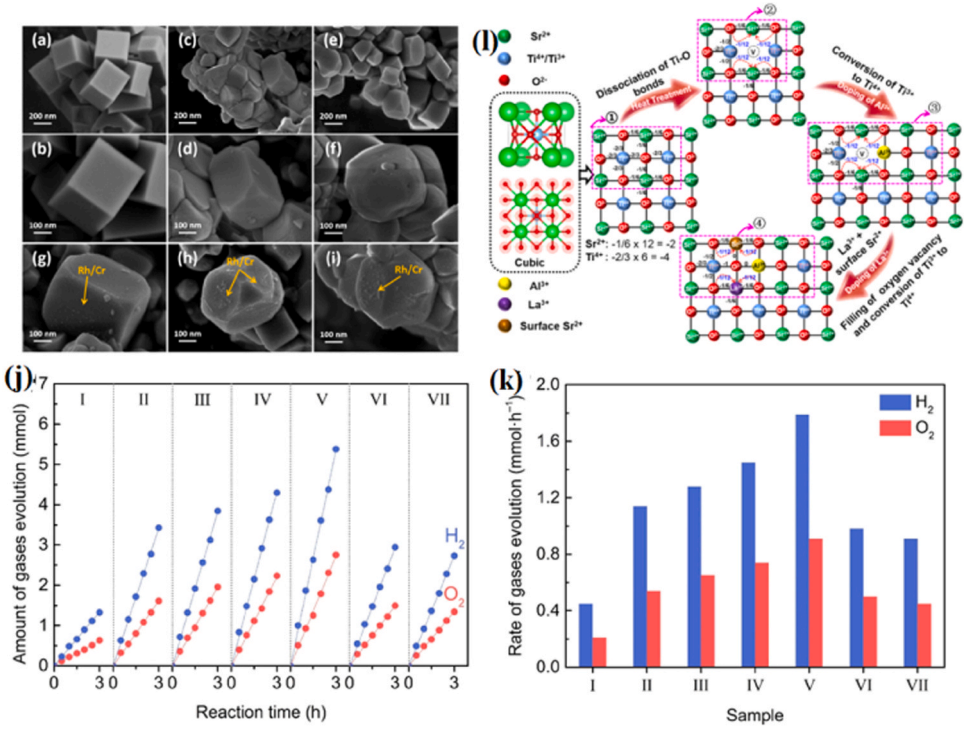


Fig. 10. SEM images of (**a,b**) $SrTiO_3$, (**c,d**) Al(1.0)-$SrTiO_3$, and (**e,f**) La,Al(0.6,1.0)-$SrTiO_3$; and (**g**—**i**) La,Al(0.6,1.0)-$SrTiO_3$ loaded with Rh(0.1%wt)/Cr(0.05%wt)/Co(0.05%wt). (**j**) Typical time course profiles corresponding to hydrogen and oxygen evolutions, (**k**) Corresponding photocatalytic rates [(I) pure $SrTiO_3$, (II) Al(1.0)-$SrTiO_3$, (III) La, Al (0.2,1.0)- $SrTiO_3$, (IV) La, Al (0.4, 1.0)- $SrTiO_3$, (V) La, Al (0.6,1.0)- $SrTiO_3$, (VI) La, Al (0.8, 1.0)- $SrTiO_3$, and (VII) La, Al (1.0, 1.0)- $SrTiO_3$]. (**l**) Schematic of lanthanum- and aliovalent-codoped $SrTiO_3$. Reprinted with permission, copyright, 2021, American Chemical Society [89].

absorption of visible light comprising of 39% of solar spectrum [176–178], (ii) the utilization of incident light by trapping and extending the optical length [179,180]. Recently, hollow multishell structures and hierarchical voids were reported as ideal candidates for efficient photocatalytic performances [90,181–184]. TEM, SEM and corresponding XRD results of the recently reported $SrTiO_3$:La/Rh hollow single shelled and $SrTiO_3$:La/Rh HoMSs double-shelled structures are shown in Fig. 11**(a-f)** [91]. The synthesis procedure of $SrTiO_3$-based HoMSs is shown in Fig. 11**g**. Its excellent efficiency towards hydrogen production, outstanding long-term performance, reusability and

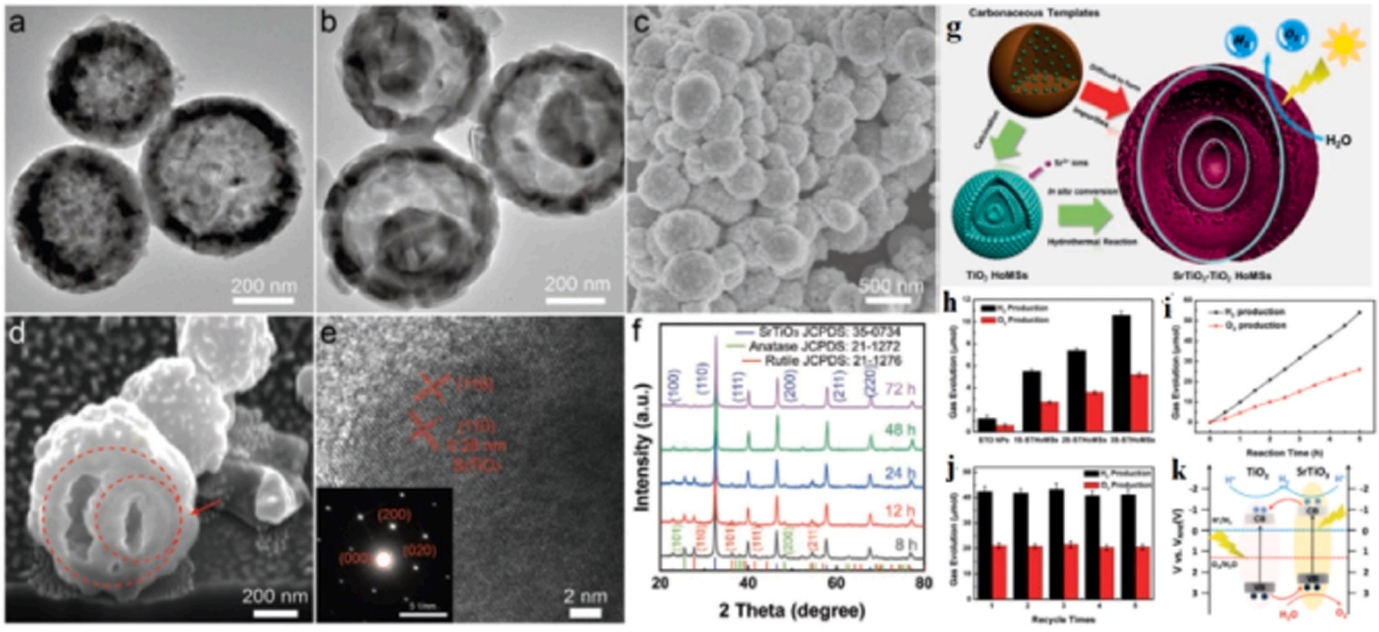


Fig. 11. HRTEM images: **(a)** $SrTiO_3$:La/Rh hollow structure, and **(b)** $SrTiO_3$:La/Rh HoMSs, **(c)** SEM image of $SrTiO_3$:La/Rh HoMSs, **(d)** Cross-sectional SEM of $SrTiO_3$:La/Rh HoMS, **(e)** HRTEM, and SAED of $SrTiO_3$:La/Rh HoMSs, **(f)** XRD of $SrTiO_3$:La/Rh HoMSs. Reprinted with permission, copyright, 2021, John Wiley and Sons [91], **(g)** Synthesis route of $SrTiO_3$ @TiO_2 HoMSs from the hydrothermal reaction, **(h)** Photocatalytic overall water splitting performance, **(i)** Time course profiles corresponding to hydrogen and oxygen evolution by water splitting under 300 W Xe lamp irradiation. **(j)** Durability of $SrTiO_3$ HoMSs in overall water splitting. **(k)** Possible band structure diagram of $SrTiO_3$ HoMSs. Reprinted with permission, copyright, 2019, John Wiley and Sons [90].

possible mechanism is shown in Fig. 11(**g-k**), respectively [90]. Thus, the recent study of structural engineering in $SrTiO_3$ based HoMSs demonstrates potential designs to enhance the competence by extending the absorption range to the visible region.

6.5. Long term stability & efficiency towards commercialization

Long-term stability towards hydrogen generation is one of the most challenging barriers to be addressed for commercial applications. QE and durability over prolonged operation periods at ambient pressure are very much important for fulfilling the requirements for practical applications [185]. Wang et al. reported the $SrTiO_3$-based photocatalytic system with remarkable solar-to-hydrogen energy conversion efficiency [156]. Besides, under UV light irradiation, the lanthanum-doped $NaTaO_3$ photocatalytic system showed 16 days of stability with continuous water splitting activity [186]. Another study with GaN:ZnO solid solution loaded with rhodium chromium oxide evolved hydrogen via water splitting up to three months under visible light, even though a photocatalytic activity loss of 50% was observed with time [187]. Lyu et el. reported Al-doped $SrTiO_3$ loaded with $RhCrO_x$ cocatalyst for efficient water splitting with high AQE above 50% [92]. Further, photodeposition of CoOOH and TiO_2 enhanced the AQE up to 80% activity and a solar-to-hydrogen energy conversion above 0.3% for 1300 h corresponding to 54 days under simulated sunlight (Fig. 12**a**). The role of CoOOH in $RhCrO_x/SrTiO_3$:Al surface is represented in Figs. 12**b** and 12**c**. Further development of modified robust $SrTiO_3$-based photocatalysts for water splitting can overcome a longstanding barrier in commercial sunlight-driven hydrogen generation.

6.6. Large-scale solar hydrogen generation

Various strategies have been adopted for cost-effective and greener hydrogen generation. The combination of photovoltaic cells with external electrolyzers and PEC cells showed high solar-to-hydrogen energy conversion efficiency [188,189]. A 12% solar-to-hydrogen energy conversion efficiency corresponding to a perovskite photovoltaic cell and a PEC cell consisting of an anolyte and a catholyte parted with bipolar membrane was demonstrated by Luo et al. [189]. Further, this efficiency was boosted up to 30% with polymer electrolyte membrane electrolyzers linked to an In- GaP/GaAs/GaInNAsSb triple-junction solar cell in series [188]. This was limited in small-to-scale research while few concepts were proposed for scaling-up of these technologies [190]. A recent analysis suggests photocatalytic water splitting as an effectual and potentially ascendable and economic strategy towards solar hydrogen generation [191]. Poor photocatalytic efficiency towards water-splitting upon sunlight irradiation is the main difficulty for scaling up the experiment [192]. Schröder et al., developed successfully a panel-type reactor with a carbon nitride photocatalytic system restrained on a stainless steel substrate, accomplishing a maximum solar-to-hydrogen conversion efficiency of 0.12% towards photocatalytic HER [193]. Recently, a sunlight driven large-scale, and commercially viable water splitting reactor with an Al-doped $SrTiO_3$ photocatalytic system was proposed (Fig. 13), wherein a 0.4% STH efficiency was achieved [44].

7. Summary and outlook

Solar hydrogen generation by water splitting is a sustainable and competitive approach to compensate all the environmental and energy related problems because of fossil fuel consumption and its scarcity. However, to make the solar hydrogen generation more economic, novel and unique photocatalytic systems need to be explored. $SrTiO_3$ is one of the most promising and widely explored materials for various applications in the modern science era. However, inclusive reviews based on the applications of $SrTiO_3$ systems for photocatalytic applications especially for hydrogen generation via water splitting are not much available. Additionally, and most interestingly, various fundamental approaches have been carried out recently to commercialize the usage of $SrTiO_3$-based photocatalysts, hence symbolizing the demand of the current review to substantiate the necessity of $SrTiO_3$ in the photocatalysis field.

The implementation of $SrTiO_3$-based photocatalysts for hydrogen generation applications is elaborated systematically. Initially, a historical background and advances of the $SrTiO_3$ based catalytic systems, their crystal structure and properties along with fundamental and thermodynamic aspects of photocatalytic HER via water splitting with $SrTiO_3$ system are discussed. Subsequently, for enhancing the overall performance and thereby overcoming the major challenges faced by $SrTiO_3$ photocatalytic systems are elaborated more critically, we summarized several innovation strategies including band gap engineering, heterojunction building, surface engineering, defect engineering, nano structuring and regulating the morphological features.

A detailed literature survey on fine tuning of the properties of $SrTiO_3$ has demonstrated enhanced photon absorption characteristics favorable for the accomplishment of high photocatalytic activity towards hydrogen generation. Different architectural materials for enhanced photocatalytic performance towards water splitting have been reported

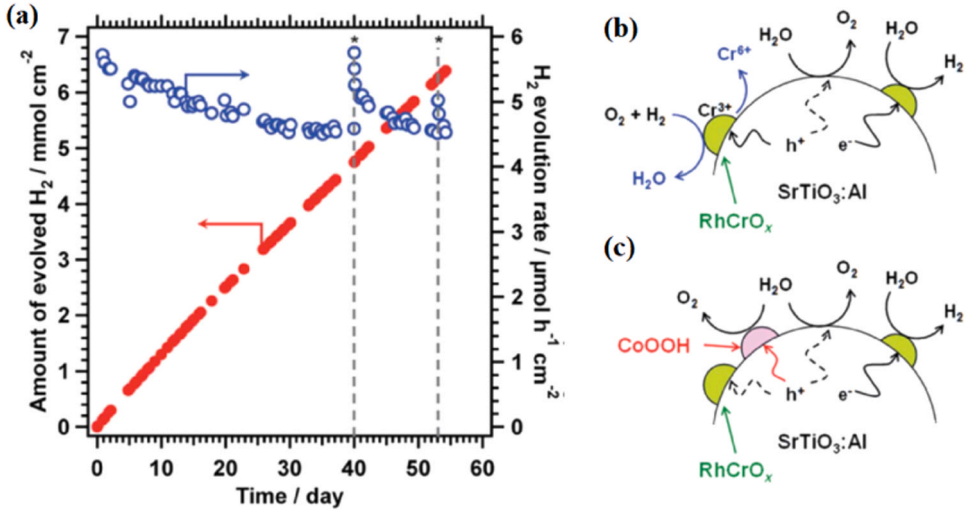


Fig. 12. **(a)** Water splitting activity of 5 × 5 cm^2 TiO_2/CoOOH/$RhCrO_x$/$SrTiO_3$:Al sheet in panel reactor. Illustrations corresponding to **(b)** deactivation of $RhCrO_x$/$SrTiO_3$:Al and **(c)** stabilization mechanism by CoOOH. Reprinted with permission, copyright, 2019, Royal Society of Chemistry [92].

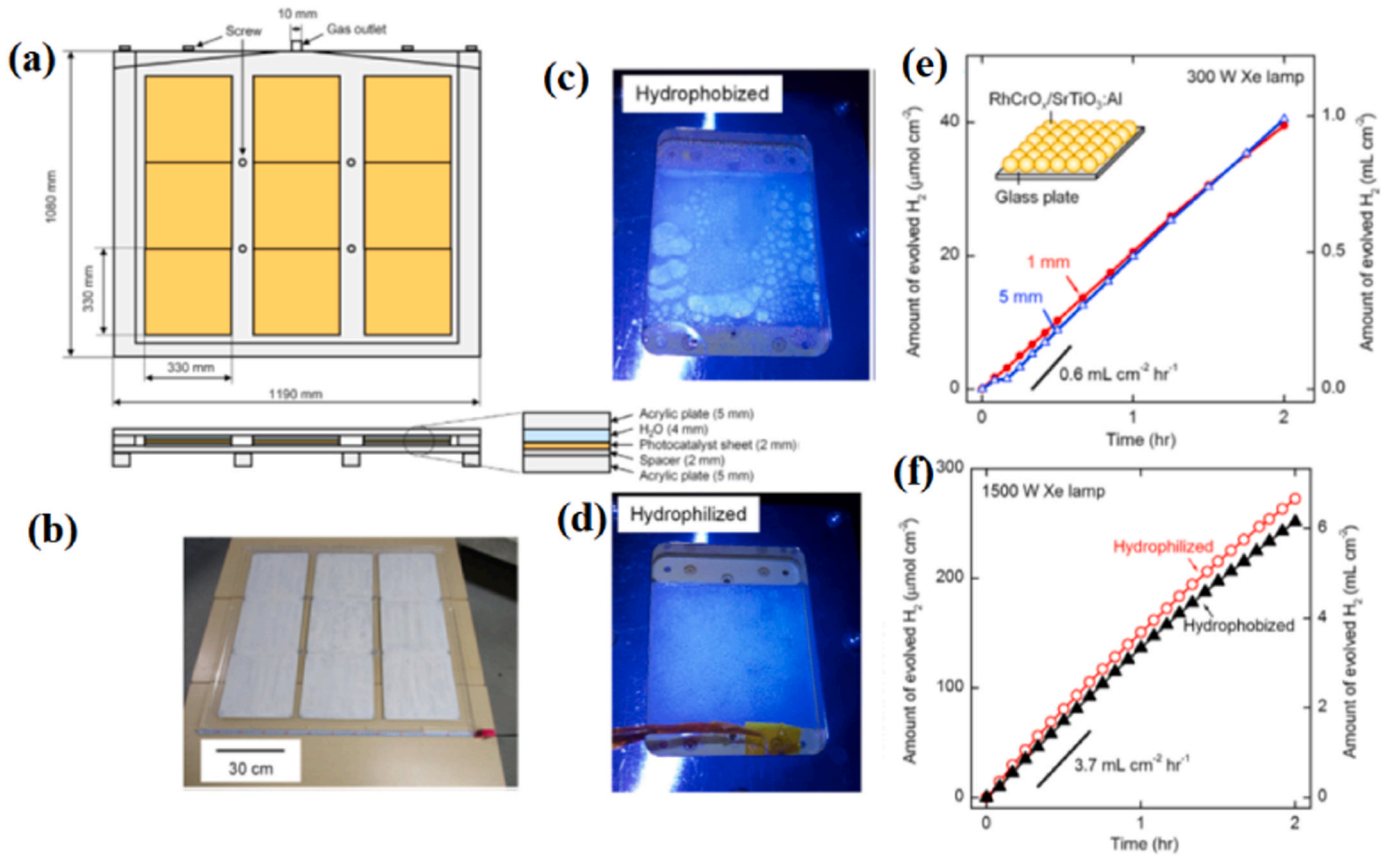


Fig. 13. **(a)** Water-splitting panels containing 33 × 33 cm of nine $SrTiO_3$:Al sheets, wherein the window used is that of a hydrophilized acrylic plate, 10° tilt ~ 4 kg weight. **(b)** Photographic image of $SrTiO_3$:Al panel (1 m x 1 m). (**c** and **d**) Photograph of $SrTiO_3$:Al panel (1 m x 1 m) while light irradiation via hydrophilized and hydrophobized opening. **(e)** Water splitting by 5 × 5 $SrTiO_3$:Al panels at dissimilar water depths of 1 mm and 5 mm under 300 W Xe lamp. **(f)** Water splitting by 5 × 5 $SrTiO_3$:Al panels with hydrophilized or a hydrophobized quartz window in 1 mm water depths under 1500 W Xe lamp. Gas evolution rate was initially attuned to a 10% solar to hydrogen value. Reprinted with permission, copyright, 2018, Elsevier [44].

through economical and facile strategies, among which binary systems such as of $SrTiO_3$. Al loaded with Rh, Cr and Co cocatalysts are found to be more fascinating photocatalysts for HER with quantum efficiency of almost unity. Further, various strategies of surface engineering $SrTiO_3$ heterostructures with plasmonic metals such as Au, Ag, and Cu nanoparticles are discussed as truly inspiring for achieving enhanced plasmon induced water splitting performance. Along with surface engineering, the consequences of defect engineering towards HER performance are also evaluated in corresponding sections with recent case studies of doping $SrTiO_3$ with low valence metal cations. Even though several promising photocatalytic systems have been reported, there are still several major challenges to be addressed, especially poor light absorption, surface shielding, blockage of surface-active sites owing to excessive cocatalyst loading, possibility of surface back reactions, etc. So, the design strategy of modelling unique complex multishelled structured photocatalytic systems as an attempt to overcome the major challenges to an extent is analyzed in the following section. Recently single-shelled $SrTiO_3$:La/Rh hollow structures and double-shelled $SrTiO_3$:La/Rh hollow multishell structures (HoMSs): were reported as efficient photocatalytic systems towards hydrogen generation with pronounced light harvesting ability and extended absorption characteristics. For large scale applications, quantum efficiency and long-term stability are crucial factors to be addressed. $RhCrO_x/SrTiO_3$:Al photodeposited with CoOH and TiO_2 was reported to be highly competing for long term sunlight driven hydrogen generation.

Despite the significant advancement in photocatalytic hydrogen generation, the economic competency of solar hydrogen generation still remains as a major challenge under critical scrutinization. To substantiate high efficiency of small-scale solar hydrogen generation, and further to compensate fatalities in catalytic efficiency owing to inappropriate outdoor temperatures, thermally coupled devices free of membranes must be fabricated. Such methodologies can be applied worldwide in remote regions for the fabrication of excellent thermally coupled solar water splitting based on perovskite materials. $SrTiO_3$-based catalytic systems being well established among perovskites type photocatalysts can be implemented in fabricating such devices with tandem cells for sustained and long-term hydrogen generation. The main concern to be addressed is whether this approach can be favored at higher levels of device amalgamation with several designs. Moreover, device efficiency and consequences need to be critically scrutinized at various altitudes worldwide during a particular year duration. The efficiency has to be monitored by combining various in situ techniques and computation modelling tools. Such outdoor device fabrication strategies compared to other photovoltaic technologies could reduce the photocatalyst loading amount significantly and the probability of scaling up solar hydrogen generation at global scale increases. In addition, another major bottleneck issue is water oxidation to molecular oxygen. This can be overcome by implementing homogenous oxygen evolution catalysts, hence the concept of ideal photocatalysts is not that difficult to identify and this could enable water splitting a more facile and economic process.

Overall, this review is expected to offer a new milestone as a translational approach towards the supply of fossil fuel free energy and would provide more insights in decarbonizing the energy. This can become a considerable contribution towards the global decarbonization of the energy sector.

CRediT authorship contribution statement

A.H. and T.C.B.: Writing — original draft, Writing – review & editing; E.A.M.: Managing graphics and figures; A.M.A.H and Y.M.: Writing – review & editing. A.V.S. and S.M.A.S.: Supervision.

Declaration of Competing Interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome. We also confirm that the manuscript has been read and approved by all named authors, and the order of authors listed in the manuscript has been approved by all named authors.

Data Availability

The authors are unable or have chosen not to specify which data has been used.

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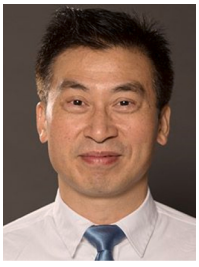

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